

PATENT SPECIFICATION

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(54) METHOD FOR THE PRODUCTION OF A HYDROPHILIC POLYURETHANE FOAM

SPECIFICATION NO 1354576

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of FRITZ NAUER AG, a Swiss Company of Im Kreuz, CH-8712 Staefa, Switzerland.

THE PATENT OFFICE

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- 10 proved method for the production of a hydro-
 philic polyurethane foam by reacting polyols
 containing ether groups (polyether polyols)
 with polyisocyanates in the presence of at least
 one foam stabilizing agent and at least one
 15 catalyst by the so-called "one-shot" tech-
 nique. Furthermore, the present invention also
 relates to the product obtained by the afore-
 said inventive method as well as to a par-
 ticular use of the method of the invention.
 20 It is known to the art to produce soft
 foam materials possessing urethane groups
 from linear and/or branched polyols contain-
 ing ether groups, primarily diols, and poly-
 isocyanates, especially diisocyanates, in the
 25 presence of propellants such as water and fur-
 ther adjuvants. These adjuvants or auxiliary
 substances serve the purpose of facilitating
 the formation of the foam or prevent a col-
 lapse of the foam upon completion of the
 30 gas forming reaction. Such are the so-called
 foam stabilizing agents, as for instance, organo-
 polysiloxane-polyalkylene glycol ethers, soaps,
 and ethoxylated fatty acid esters. Further ad-
 35 juvants are catalysts which ensure that the
 operations occurring during foam formation
 proceed generally and in relation to one
 another with the proper speed.

- 40 The polyurethane foams produced accord-
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 is by mixing together all of the components and
 immediate discharge thereof, have found wide-
 spread use in industry, the household and in

Another more specific object of the present
 invention is the provision of a new and im-
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Yet a further significant object of the pre-
 sent invention relates to an improved method
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 55 thane foam.

Natural as well as viscous sponges, sponge-
 like cleaning rags, which can also contain
 peptide-like materials, and leather (deerskin)
 are hydrophilic to the extent that they are
 capable of absorbing water from a wet sur-
 60 face. The same holds true for polyurethane
 sponges. The absorption of water is predicated
 upon the presence of voids and capillaries.
 However, it is not possible to wipe completely
 dry a wet surface with an already wet sponge
 or leather cloth. A certain residual amount
 of water tends to remain upon the surface.
 65 This is generally known, so that industry has
 been forced to develop drying liquids —
 generally on the basis of methanol — which
 must be sprayed upon the surfaces which
 are to be completely dried, especially win-
 70 dows, mirrors, and automobile bodies. Yet the
 use thereof is expensive and not without dam-
 aging effects to varnish and paints.

Attempts have already been undertaken to
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(54) METHOD FOR THE PRODUCTION OF A HYDROPHILIC
 POLYURETHANE FOAM

(71) We, FRITZ NAUER & CO., of Im Kreuz, Stafa, Zurich, Switzerland, a Swiss company, a Kommanditgesellschaft, do hereby declare the invention, for which we pray that

a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved method for the production of a hydrophilic polyurethane foam by reacting polyols containing ether groups (polyether polyols) with polyisocyanates in the presence of at least one foam stabilizing agent and at least one catalyst by the so-called "one-shot" technique. Furthermore, the present invention also relates to the product obtained by the aforesaid inventive method as well as to a particular use of the method of the invention.

It is known to the art to produce soft foam materials possessing urethane groups from linear and/or branched polyols containing ether groups, primarily diols, and polyisocyanates, especially diisocyanates, in the presence of propellants such as water and further adjuvants. These adjuvants or auxiliary substances serve the purpose of facilitating the formation of the foam or prevent a collapse of the foam upon completion of the gas forming reaction. Such are the so-called foam stabilizing agents, as for instance, organopolysiloxane-polyalkylene glycol ethers, soaps, and ethoxylated fatty acid esters. Further adjuvants are catalysts which ensure that the operations occurring during foam formation proceed generally and in relation to one another with the proper speed.

The polyurethane foams produced according to the so-called "one-shot" technique, that is by mixing together all of the components and immediate discharge thereof, have found widespread use in industry, the household and in

maintenance- and cleaning establishments. A noteworthy drawback of all of the prior art foam materials, even those which are not polyurethanes, is their hydrophobic properties.

Accordingly, a real need exists in the art for a foam material which does not possess the aforementioned disadvantages of the prior art products. Hence, a primary objective of this invention is to effectively fulfill this need.

Another more specific object of the present invention is the provision of a new and improved hydrophilic polyurethane foam.

Yet a further significant object of the present invention relates to an improved method for the fabrication of a hydrophilic polyurethane foam.

Natural as well as viscous sponges, sponge-like cleaning rags, which can also contain peptide-like materials, and leather (deerskin) are hydrophilic to the extent that they are capable of absorbing water from a wet surface. The same holds true for polyurethane sponges. The absorption of water is predicated upon the presence of voids and capillaries. However, it is not possible to wipe completely dry a wet surface with an already wet sponge or leather cloth. A certain residual amount of water tends to remain upon the surface. This is generally known, so that industry has been forced to develop drying liquids — generally on the basis of methanol — which must be sprayed upon the surfaces which are to be completely dried, especially windows, mirrors, and automobile bodies. Yet the use thereof is expensive and not without damaging effects to varnish and paints.

Attempts have already been undertaken to increase the hydrophilic properties of polyurethane foam. Thus, for instance, hydrophilic polyol components or salt-like additives were used in the reaction mixture. Although such additives tended to initially increase the hydro-

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philic properties such became lost after about twenty-four to forty-eight hours, because secondary reactions occurred in the foam.

5 A second possibility for increasing the hydrophilic properties of the foam resides in the use of a chemical after-treatment, for instance by grafting hydrophilic compounds or by modifying the foam structure itself. Yet this possibility is prohibitive for economical reasons and apart from such, did not provide reproducible results.

10 Finally, it has already been proposed for quite some time to add to the reaction mixture cellulose and/or its derivatives, especially cellulose esters and ethers. However, since a large portion of these materials are entrapped by the hydrophobic polyurethane during formation of the foam, it was necessary, in order to obtain sufficient hydrophilic properties of the foam, to use such large quantities of these materials that the physical characteristics of the foam assumed unacceptable values.

20 Extensive experiments have now led to the result that it is possible to obtain a completely hydrophilic polyurethane foam possessing exceptional physical properties, especially strength, if there is used a certain, hereinafter to be defined polyether polyol component as well as a special additive for the reaction mixture, and moreover, if during the foaming step certain process parameters are controlled.

30 According to the present invention, there is provided a method for the preparation of a hydrophilic polyurethane foam, wherein a polyether polyol component is reacted by the one-shot technique with an organic polyisocyanate component in the presence of a catalyst for the urethane formation and a catalyst for the propellant formation, at least one foam stabilizing agent, and water serving to form the CO₂ propellant, the improvement comprising, in combination,

- 45 (1) using, as the polyether polyol component, a mixture of a) 30 to 100% by weight of the addition product of 35 to 100 moles of ethylene oxide or a mixture of ethylene oxide and propylene oxide, the ethylene oxide representing the major amount of this mixture, to 1 mole of an aliphatic diol or a mixture of an aliphatic diol and an aliphatic triol, the diol representing the major amount of this mixture, and b) 0 to 70% by weight of a polyether polyol having branched chains and derived from an aliphatic triol,
- 50 (2) adjusting the reaction mixture to have an equivalent weight ratio of the polyisocyanate component to the polyol component of (80 to 105): 100, and
- 60 (3) adding an inert vapourizable liquid to the one-shot reaction mixture in amounts to prevent the temperature at any point in the forming foam block from exceeding

120° C during the entire time of foam preparation. 65

As the polyol component for the polyurethane foam to be produced according to the invention, there is used 30% to 100%, based upon the weight of the polyol component, of the mentioned highly hydrophilic addition compound (a). This is preferably obtained from ethylene glycol or propylene glycol, which may contain a minor amount of glycerol, and with which there is reacted the ethylene oxide or a mixture of ethylene oxide and propylene oxide wherein the ethylene oxide is the major constituent. Other aliphatic diols coming under consideration are trimethylene glycol, diethylene glycol, dipropylene glycol, butane-1,3-diol, butane-1,4-diol, bis-(hydroxymethyl)-cyclohexane, and further glycol ethers. The mentioned polyol component provides a polyether with terminal OH-groups possessing at least two and not more than three free OH-groups per molecule. In the event the described polyether polyol is not used as the sole polyol, then, as a rule, such is employed in mixture with another polyether polyol. Preferred, is a polyether polyol with a marked branched chain formed on the basis of an aliphatic triol, which is etherized with propylene oxide or mixtures of propylene oxide and ethylene oxide.

95 Preferably, component (a) of the polyol mixture is the addition product of 35 to 100 moles, especially 45 to 65 moles, of ethylene oxide to 1 mole of ethylene glycol, said addition product having a molecular weight of 1500 to 2200 and hydroxyl number of 50 to 60, and component (b) is the addition product of propylene oxide to an aliphatic triol, e.g., glycerol. 100

For the polyisocyanate component there can be employed the compounds which are known for this purpose. Suitable examples are: toluylene-2,4-diisocyanate, toluylene-2,6-diisocyanate, mixtures of both of these substances, diphenylmethane-1,3-diisocyanate, naphthylene-1,5-diisocyanate and naphthylene-1,4-diisocyanate, hexamethylene diisocyanate, dimeric toluylene-2,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, cyclohexane-1,4-diisocyanate, 4,4',4''-triphenylmethane-triisocyanate, and polymethylene polyphenyl isocyanate with 3 to 6 benzene rings. However, it is preferred to use the toluylene diisocyanates as pure compounds or as mixtures of isomers. 115

The foam stabilizers and catalysts which are to be used are well-known in the technology of polyurethane foam fabrication. The so-called propellant reaction, responsible for the weight per unit volume and the porosity of the foam, is generally catalysed by tertiary amines such as triethylene diamine or tetramethylbutane diamine. Suitable catalysts for the cross-linking reaction which determines the strength of the foam, are organometallic compounds such as stannic dioctoate or stannic 125

dilaurate. Coming under consideration as the foam stabilizers are ethoxylated silicone-containing substances, for instance water soluble organopolysiloxane-polyalkylene glycol ethers, to which there are generally added emulsifying agents such as sulfonated castor oils, alkylene oxide-adducts formed by reacting hydrophobic substances containing hydroxyl-and/or amino groups, and soaps. Further adjuvants are fillers, dyes, and plasticizers.

An essential aspect of the invention is the equivalent ratio of polyisocyanate to polyol. This is conventionally referred to as the "urethane index" or, in the case of toluylene diisocyanate, as the "TDI-index or value". This index or value indicates the number of isocyanate groups in the reaction mixture per 100 OH-groups of the polyol component having reactive H-atoms. According to the invention, the urethane index amounts to 80 to 105, and preferably is retained beneath 100, e.g. between 90 and 99.5. Since the propellant water decomposes a portion of the isocyanate groups free hydroxyl groups in the urethane molecules appear in the finished foam, and they probably contribute to the exceptional hydrophilic properties of the product.

A further essential feature of the invention, particularly the inventive method or process, resides in controlling the temperature during preparation of the foam. It is known that the urethane formation from isocyanate groups and hydroxyl groups and the reaction of isocyanate with water with the formation of CO_2 (propellant reaction) are exothermic reactions. A considerable temperature increase in the produced strand-like foam blocks appear by virtue of the exothermic reactions, since the foam basically acts as a heat insulator. The temperature increase in the generally employed "one-shot" technique, and also employed in accordance with the invention, is greater than that for the so-called "two-shot" technique or process working with a prepolymer.

Generally, with foam blocks having a cross-section of 0.25 to 1 m^2 , the temperature at the interior of the blocks climbs to 140° C. to 160° C. and can reach as much as 220° C. At these temperatures, side reactions are favored, especially the so-called biuret- and allophanate reactions. It has now been found that the hydrophilic property of the foam is markedly reduced by these side reactions. Among other things, this has been shown by virtue of the fact that the cooler external regions of the foam block, during the foaming operation, were hydrophilic and after about forty-eight hours lost their hydrophilic characteristics, whereas the inner regions, even at the beginning of the manufacturing operation, only possessed a very weak hydrophilic property.

According to the invention, temperature regulation is undertaken by means of a cooling agent admixed to the reaction mixture

prior to foaming. To this end, there is employed an inert vaporizable liquid. During the formation of the foam, this liquid absorbs a portion of the reaction heat and vaporizes. In this way, there is possible a very good temperature regulation because during the pronounced formation of heat there occurs a pronounced vaporization, that is, a pronounced consumption of heat.

As the cooling liquid, there are preferably employed organic compounds with as high as possible heat of vaporization and a boiling point accommodated to the conditions of the reaction. Particularly suitable are halogenated hydrocarbons, such as dichloromethane, dichlorodifluoromethane, trichlorofluoromethane, dichlorofluoromethane, chloroform, trichlorotrifluoroethane, and dichlorotetrafluoroethane. By using mixtures, it is possible to achieve an even more flexible accommodation to the cooling requirements and a stepwise cooling.

Although some of the heretofore exemplary mentioned cooling agents have already been used as propellants in polyurethane foams, in the inventive process water exclusively serves as the propellant, that is to say, the thus generated CO_2 . It was previously unknown and not obvious to control only the progress of the temperature during foaming by means of the mentioned compound. Additionally, cooling agents are suitable which are unsuitable as propellants.

By virtue of the inventive method, it is possible to obtain excellent solid, yet flexible foams, possessing hydrophilic properties to a degree heretofore unknown. It is even possible to completely dry-wipe a wet surface with a rag formed from or peeled-out of the foam material even when in wet condition; something that previously was not possible. Heretofore, there was always present an equilibrium condition between the quantity of water upon the substrate and in the foam or cleaning cloth, so that a certain quantity of water, which even in the most favorable condition was quite small, remained upon the substrate, and which was noticeable as a film and in the form of droplets. In the following examples, there have been listed appropriate characteristic values.

The hydrophilic property can be still further improved whereby the foam simultaneously becomes swellable during sucking of water, if there is added to the reaction mixture as a swelling agent an inorganic silicate possessing a laminar structure, for instance montmorillonite, bentonite, and lithium-sodium-magnesium-fluosilicates, in quantities up to 20 parts by weight for 100 parts of the polyol component. This swelling agent incorporates into the cellular wall of the foam, but is, however, only weakly wetted by the foam, so that it is not completely included into the foam mass.

The polyurethane foam fabricated accord-

ing to the method of the invention is suitable for further processing into cleaning cloth or rags, since it possesses relatively fine pores. However, if it is desired to form a foam from the aforementioned reaction mixture, which is suitable as the raw material for cleaning sponges having an appearance similar to natural sponges, then it is necessary to add a further adjuvant, a so-called cell destructor. This adjuvant is known; it causes the uniting of the capillaries into larger alveoles, without the foam structure itself being destroyed and without loss of the microporosity of the cell walls.

It has been observed that the previously employed silicone-containing pastes or emulsions resulted in a considerable loss of the hydrophilic characteristics.

It has now been found that by admixing with the reaction mixture a novel adjuvant of a combined swelling agent and cell destruction agent, these drawbacks can be completely overcome. The novel adjuvants consist of a powder formed of cellulose, a cellulose derivative or another porous carrier, which can be of organic or inorganic nature, containing an organic silicon compound (a silicone) which is highly thinned and finely distributed. Production of the novel adjuvant or auxiliary agent will be explained hereinafter in conjunction with an example.

Preferably, the reaction mixture for producing the inventive polyurethane foam thus contains the following constituents, the quantitative range of which is likewise indicated:

1. Polyether polyol component:
 - (a) a mixture of 30 to 100% by weight of addition product of 35 to 100 moles of ethylene oxide or a mixture of ethylene oxide and propylene oxide, the ethylene oxide representing the major amount of this mixture, to 1 mole of an aliphatic diol or a mixture of an aliphatic diol and an aliphatic triol, the diol representing the major amount of this mixture, and
 - (b) 0 to 70% by weight of a polyether polyol having branched chains and derived from an aliphatic triol;
2. Polyisocyanate component:

As many parts to obtain an equivalent weight ratio of the polyisocyanate component of (80 to 105):100, preferably (90 to 99.5)/100;
3. Swelling agent on the basis of inorganic Li-Na-Mg-fluorosilicates ("Makaloid", a trade mark of Inerto Co., Las Vegas, USA) or montmorillonite: 0 to 20 parts;
4. Propellant (water): 1.5 to 3.5 parts;
5. Propellant catalyst: 0.1 to 1 part;
6. Urethane catalyst: 0.05 to 1.5 parts;
7. Foam stabilizers: 0.8 to 2.5 parts;

8. Coolant:

As many parts as are necessary to achieve a maximum temperature in the foam of 120° C, preferably 90° C to 110° C, approximately 5 to 20 parts.

In order to produce foam materials which are to be used as sponges, there are further added the already mentioned additional components (silicone-containing cellulose and cellulose derivative) and specifically dispersed in component 1. From such a dispersion which contains 1% by weight cellulose and 0.28% by weight of the silicone, there is used for 100 parts of the component 1 given in the above table 0.5 to 2 parts. Air is dispersed in known manner in the reaction mixture in order to further fluff or loosen the sponge.

Further details with regard to the performance of the method need not be explained as they will be readily apparent to those versed in the art.

Method Example.

The method of the invention which is to be explained is carried out in a conventional foam fabricating machine possessing as its major components a mixing and settling head moving to and fro over the width of the foam block, an ascending tunnel with a suction device and a post- or after reaction path. The conveyor band for the foam moves with a velocity of about 1.5 meters/minute to 5 meters/minute. The resultant foam block, approximately 1 meter to 2 meters wide and 0.5 to 0.8 meters high, is cut-up into blocks at the end of the after reaction path.

Example 1.

The mixing- and settling head of the foam fabricating installation has delivered thereto per unit of time the following substances in the hereinafter given quantities, with the parts representing parts by weight:

1. (a) Highly ethoxylated polyether diol on the basis of ethylene glycol, approximately 65 ethoxy groups per molecule, OH-number=56, M (molecular weight)=2200; 90 parts (available from Farbenfabriken Bayer under the trade mark "DD 3002");
- (b) Strongly branched highly reactive polyether polyol, obtained by addition of propylene oxide to glycerol, M=3900, OH-number: 38 (obtainable from Farbenfabriken Bayer under the trade mark "Desmophen 3900"): 10 parts;
2. The product known as "Makaloid" (a sodium-lithium-magnesium-fluorosilicate) of Inerto Co., Las Vegas, Nevada, serving as the swelling agent: 5 parts;
3. Toluylene diisocyanate, isomer mixture 2,4 (65%) and 2,6 (35%): 28 parts;
4. Water: 2 parts;
5. Tetramethylbutanediamine: 0.6 parts;

6. Foam stabilizer (product of Farbenfabri-
ken Bayer known as "DD 3045") 1.5 parts;
7. Urethane catalyst: tin octoate, 0.4 parts;
8. Cooling agent: "Frigen 11" (trade mark
product of Farbwerke Hoechst AG) 5 parts
"Frigen 11" is trichlorofluoromethane.

The mixture discharged from the settling
head possessed a temperature of 23° C. The
urethane index of the composition amounted to
about 95. During foaming and after reaction
the temperature in the foam block climbed
to 115° C. There was obtained a completely
hydrophilic foam, the properties of which are
given hereinafter, specifically in Table 2. From
the foam material there was cut at a peeling
machine 0.8 cm. thick cleaning rags which
retained their hydrophilic properties even after
repeated washing in hot water.

Example 2 (Comparison).

(a) Components 1 to 7 of Example 1 were
used, yet component 8 was omitted. The
temperature in the foam block climbed to
165° C. The properties of the marginal por-
tions of the block, up to a depth of about
10 cm., were identical with those of the block
of Example 1. The properties at the core of
the foam material were measured immediately
during fabrication and after 72 hours. They
have been set forth in Table 2. Although the
mechanical properties and the density of this
comparison product corresponded to those of
Example 1, the hydrophilic properties,
measured by means of the wiping factor,
were insufficient.

(b) There were used components 2 to 8 of
Example 1. Instead of component 1 there was
not used a mixture, rather component 1(b)—
("Desmophen 3900") was used alone.

The properties of this comparison product
are given in Table 2 below. Although the
temperature of the foam block during fabri-
cation did not exceed 120° C., the hydrophilic
properties were insufficient.

(c) A further comparative trial was under-
taken with the same components used in
comparison Example 2(b) above, but with
the omission of the cooling agent (component
8). The temperature in the foam block climbed
to 165° C. Neither the outer nor the inner
portions of the block were hydrophilic.

Example 3.

The same procedure as in Example 1 was

followed, but with the omission of component
2. There resulted a foam material with less
swelling than that of Example 1, but with
completely sufficient hydrophilic properties;
see the values given in Table 2 hereinafter.

Example 4.

Production of Foam Material for Sponges.

(a) Preparation of a novel cell destructor or
cell destructor agent: 25 parts of an approxi-
mately 1% by weight silicone-containing paste
(for instance, trade mark products "L 501",
of Union Carbide; "Siloprenpaste K 1", Far-
benfabriken Bayer; "Silikon M 100", Far-
benfabriken Bayer) are dispersed in 25 parts
methylene chloride. Added to the dispersion,
while strongly stirring it, were 5 parts of a
carrier powder ("Celite"-type, trade mark pro-
ducts of Johns-Manville Company; diato-
maceos earth, and asbestos powder) and from
the obtained mixture the solvent- and dis-
persion agent was vaporized in vacuum.

3 parts of the thus obtained dry powder
were dispersed in a mixture containing 25
parts of the component 1(a) and 25 parts of
the component 1(b) of Example 1. An emulsi-
fying agent can be added in order to stabilize
this dispersion.

(b) Fabrication of Foam Material.

The same components given in Example 1
were delivered into the mixing compartment
of the foaming head of the foaming machine,
and there was likewise maintained the quan-
titative relationships given in such example.
Additionally, there was admixed thereto 1.1
parts of the dispersion obtained according to
Example 4(a) as well as air.

A block-like foam strand was obtained in
accordance with the mode of operation de-
scribed in conjunction with Example 1, with
the maximum temperature within the block
amounting to 100° C. The block was then cut
into individual sponges, the properties of which
have been given in Table 2 below.

(c) Comparison Trial.

The mode of operation of Example 4(b) was
combined with that of Example 2(c). A sponge
was obtained, the swelling and hydrophilic
properties of which is completely insufficient.
(See Table 2).

Examples 5 to 14.

In the following Table 1 there are given
further examples wherein in each instance
the procedure of Example 1 was employed.

TABLE I
Examples 5-14

No.	Component Designation	Example No. (Employed Quantities in Parts by Weight)											
		5	6	7	8	9	10	11	12	13	14		
1a	Highly ethoxylated polyol ¹⁾	50	40	20	40	30	20	70	70	50	50		
1b	Strongly branched polyol ¹⁾	50	60	80	60	70	80	30	30	50	50		
2	"Makaloid" (Swelling agent)	10	15	20	5	10	15	5	10	5	5		
3a	TDI 65/35 ²⁾	20.2	22.4	22.5	22.5	16.8	14.8	23.9	27.2	27.3	24.6		
3b	TDI 80/20 ³⁾	—	—	—	—	8.4	7.5	2.7	—	—	—		
4	Water	1.6	1.8	2.0	1.8	2.0	2.0	2.0	2.0	2.0	2.0		
5	Amine catalyst ¹⁾	0.8	0.6	0.7	0.7	0.6	0.7	0.6	0.5	0.6	0.6		
6	Foam stabilizer ¹⁾	1.2	1.2	1.7	1.6	1.5	1.6	1.5	1.5	1.5	1.5		
7	Urethane catalyst ¹⁾	0.28	0.32	0.38	0.4	0.2	0.4	0.24	0.28	0.3	0.35		
8	Cooling Agent ¹⁾	15	10	15	15	10	15	15	10.0	10.0	10.0		
9	Cell destructing agent ⁴⁾	—	—	—	—	—	—	—	—	1.6	1.0		

Remarks: ¹⁾ Same substance as in Example 1.

²⁾ Toluylene diisocyanate, 65% 2,4- and 35% 2,6-isomers.

³⁾ Toluylene diisocyanate, 80% 2,4- and 20% 2,6-isomers.

⁴⁾ For production of sponges; preparation is given on following pages.

Production of the Cell Destructing Agent of Examples 13 and 14.

7.5 parts "Siloprenpaste K 1" (Trademark product of Farbenfabriken Bayer) was dispersed in 7.5 parts dichloromethane. While vigorously stirring 1.5 parts cellulose flakes were added to the dispersion. A negative pressure was applied and the dichloromethane was removed while stirring or jarring, respectively.

1 part of the thus obtained dry, freely flowing powder was mixed with 50 parts of a mixture formed of the same parts of the components 1(a) and 1(b) of Table 1. Now, from the thus obtained mixture, there was used 1.6 parts for Example 13 and 1.0 parts for Example 14.

Checking the Obtained Products.

The products produced according to Examples 1 to 14 were checked or tested in respect of their most important properties in the following manner:

1. Swelling Capacity.

Testing Technique: A foam member dimensions of $10 \times 10 \times 5$ cm.) was compressed under water as far as possible for 30 seconds in order to remove the air and then permitted to expand. It was allowed to remain sub-

merged in water for a further 5 minutes and then drip-dried for 30 minutes on a sieve. Thereafter the dimensions of this member were again measured and the increase in volume was given as a percentage of the starting volume. Most of these values have been set forth in Table 2.

2. Wiping Factor.

A rectangular surface of 28×7 cm. was confined on a planar, smooth glass plate, and thereafter about 5 gms. of water was uniformly distributed.

A 5 cm. thick foam member was guided over the surface containing the water with its base surface possessing the dimensions of 14.3×7 cm. with a bearing pressure of about 6.3 gms./cm.² (bearing or contact weight 630 gms.), this operation occurring for three minutes with 180 wiping strokes per minute. The foam member previously was completely imbued with water and squeezed-out real well.

The glass plate was weighed both before and after wiping. The difference in weight corresponds to the quantity of water absorbed by the foam member; it is given in terms of the percent of the water present. Most of the results are set forth in Table 2.

TABLE 2

Property Values

Example No.	Weight Per Unit Volume kg/m ³	Swelling Capacity % Volume Increase	Wiping Factor %
1	28	45	95
2a *)	—	—	60
2b *)	28	—	60
2c *)	28	2.5	45
3	—	30	75
4b	28	50	90
4c *)	28	5	40
12 **)	—	—	80
X *)	28	—	50

*) Comparative trials X = Polyurethane foam subsequently rendered hydrophilic

***) Urethane index 101

The surprising properties of the new product will be readily recognized from Table 2. It is to be observed that the wiping factor was measured at samples which were previously imbuéd or wetted; with dry samples these values are all higher, but in the first instance such is attributable to the capillary action and not the hydrophilic properties. The above values approximate those found in actual practice since during use one generally works with a wet sponge.

The polyurethane foam produced according to Example 1 or Examples 5 to 12 can be further processed into deerskin-like cleaning cloths. To this end it is possible to proceed as follows:

1. At a conventional peeling machine or equivalent type equipment, there are cut so-called peeled mats from a foam block possessing a foam structure, produced without a cell destructing agent, in other words, not a sponge block. The mat is approximately 5 to 30 mm. thick and can be 60 to 100 meters long and up to 3 meters wide.

2. The mat is then continuously or discontinuously hot-pressed. There are employed pressures of 0.05 to 2.5 kg/cm², preferably about 0.1 kg/cm², and temperatures of 150° C to 200° C. Under these conditions the residence time is about 15 to 60 seconds.

3. The thus obtained cloth is about 3 to 5 mm. thick and more hydrophilic than the starting foam material because the pores terminating at the surface are "semi-closed" through the action of the heat-pressure treatment, that is to say, the capillary inlet has considerably narrowed, yet not completely closed. Thus, one is dealing in this instance with something similar to the fixation of a foam body in compressed condition.

A wiping factor of 98 to 100% is obtained for the thus produced cloth by proceeding in accordance with the method of Table 2 and the associated explanations.

The obtained cloth can be adhesively bonded or heat-sealed or otherwise united with a textile fabric or another reinforcing matrix, at one or both sides, in order to strengthen it, that is, for the purpose of increasing its mechanical resistance during drawing, wringing and so forth. Of course it is in no way necessary for the reinforcement material itself to be hydrophilic.

WHAT WE CLAIM IS:—

1. A method for the preparation of a hydrophilic polyurethane foam, wherein a polyether polyol component is reacted by the one-shot technique with an organic polyisocyanate component in the presence of a catalyst for the urethane formation and a catalyst for the propellant formation, at least one foam stabilizing agent, and water serving to form the CO₂ propellant, the improvement comprising, in combination,

(1) using, as the polyether polyol com-

ponent, a mixture of a) 30 to 100% by weight of the addition product of 35 to 100 moles of ethylene oxide or a mixture of ethylene oxide and propylene oxide, the ethylene oxide representing the major amount of this mixture, to 1 mole of an aliphatic diol or a mixture of an aliphatic diol and an aliphatic triol, the diol representing the major amount of this mixture, and b) 0 to 70% by weight of a polyether polyol having branched chains and derived from an aliphatic triol,

(2) adjusting the reaction mixture to have an equivalent weight ratio of the polyisocyanate component to the polyol component of (80 to 105):100, and

(3) adding an inert vaporizable liquid to the one-shot reaction mixture in amounts to prevent the temperature at any point forming foam block from exceeding 120° C during the entire time of foam preparation.

2. The method as defined in claim 1, wherein the polyol component is the addition product of 35 to 100 moles of ethylene oxide to 1 mole of ethylene glycol, said addition product having a molecular weight of 1500 to 2200 and a hydroxyl number of 50 to 60.

3. The method as defined in claim 2, wherein the addition product contains 45 to 65 moles of ethylene oxide per mole of ethylene glycol.

4. The method as defined in claim 1, wherein the polyol component is a mixture of

(a) the addition product of 35 to 100 moles of ethylene oxide to 1 mole of ethylene glycol, said addition product having a molecular weight of 1500 to 2200 and a hydroxyl number of 50 to 60, and

(b) the addition product of propylene oxide to an aliphatic triol.

5. The method as defined in claim 4, wherein the addition product (a) contains 45 to 65 moles of ethylene oxide per mole of ethylene glycol.

6. The method as defined in claim 1, wherein the equivalent weight ratio between the isocyanate groups and the reactive hydroxyl groups of the polyol component is maintained in the range of 90 to 99.5.

7. The method as defined in claim 1, wherein the major constituent of the polyisocyanate component is toluylene-2,4-diisocyanate, toluylene-2,6-diisocyanate, or mixtures thereof.

8. The method as defined in claim 1, wherein 5 to 20 parts by weight of the inert vaporizable liquid is used for each 100 parts by weight of the polyol component.

9. The method as defined in claim 8, wherein the inert vaporizable liquid is dichlorodifluoromethane or trichlorofluoro-

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methane, the amount of which is selected such that the temperature at any point of the prepared polyurethane foam block does not exceed a temperature in the range of 100 to 110° C.

5 10. The method as defined in claim 1, wherein further a swelling agent being montmorillonite or an inorganic lithium-sodium-magnesium-fluorosilicate is added to the one-shot reaction mixture, in an amount of up to 20 parts by weight for 100 parts of the polyol component.

15 11. The method as defined in claim 1, for the preparation of a sponge foam, wherein a cell destructing agent having swelling properties is further added to the one-shot reaction mixture.

20 12. The method as defined in claim 11, wherein the cell destructing agent is formed of an inorganic or organic porous carrier containing an organic silicon compound in fine distribution.

13. The method as defined in claim 11, wherein the cell destructing agent is added in

the form of a dispersion in a portion of the polyol component.

14. A polyurethane foam obtained according to any of the preceding claims.

15. A polyurethane foam as defined in claim 14 obtained according to the Examples.

16. A polyurethane foam as defined in claims 14 or 15, wherein such is used as a cleaning implement which is cut-out of a polyurethane foam block in mat form, possessing a thickness in the range of 5 to 30 mm., the mat having been subjected to a compression force in the range of 0.05 to 2.5 kg/cm² and a temperature in the range of 150° C to 200° C during 15 to 60 seconds.

17. The polyurethane foam as defined in claim 16, wherein the cleaning implement is adhesively bonded, at one or both sides, to a reinforcement matrix.

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